Thermoelectric Materials, Devices and Systems: Technology Assessment

Contents

1. Thermoelectric Generation

Thermoelectric materials allow for direct electricity generation through the Seebeck effect where a temperature gradient *applied to a circuit at the junction of two different conductors* produces an electromotive force based on the relation $\mathrm{E}_{\mathrm{emf}} = -S\nabla T$ where S is the Seebeck coefficient (or thermopower) (Tritt, 2011). However the use of thermoelectric modules as solid state heat pumps for heating and cooling applications using the opposite Peltier effect is far more common than their use as solid state generators (Gerard Campeau, personal communication, April 11 2014). Peltier modules, with their ability to heat and cool with great precision, have proved useful in optical equipment, automotive seats, and small consumer refrigerators. Other than fuel-burning generators that utilize thermoelectric technology to produce electricity manufactured by Global Thermoelectric and a few other companies, Seebeck generation products are rather immature.

The most common thermoelectric conductors materials today are alloys of chalcogenides (materials with a chalcogen or IUPAC group 16 anion). Specifically these materials are either based on bismuth telluride (Bi_2Te_3) or lead telluride (PbTe). Bi_2Te_3 can be alloyed with Bi_2Se_3 to form n-type $Bi_2Te_{3-x}Se_x$ and with Sb_2Te_3 to form p-type $Bi_xSb_{2-x}Te_3$. PbTe can be alloyed with PbSe to form p-type $PbTe_{1-x}Se_x$ and with SnTe to form n-type $Pb_{1-x}Sn_xTe$. PbTe has been used successfully by NASA as radioisotope thermoelectric generators (RTGs) but it has not been rejected by all current power generation projects because of the weak mechanical properties during thermal cycling from variable temperature gradient. New material classes could allow for waste heat recovery with better efficiency or use with higher temperature heat sources. These classes include skutterudites, clathrates, Half-Heuslers, and oxides such as cobaltites and perovskites (Tian, Lee, & Chen, 2013). Other material classes such as silicides (LeBlanc, Yee, Scullin, Dames, & Goodson, 2014), and tetrahedrites (Lu & Morelli, 2013) are primarily considered for their relatively low cost. These new classes have been the subject of a great deal of research but have had limited commercial use due to cost, reliability, efficiency, and processing issues that prevent them being selected over traditional materials.

A thermoelectric material's efficiency of converting heat to electricity is characterized by the dimensionless figure of merit $ZT = \frac{\sigma S^2 T}{k}$ where σ is the electrical conductivity, T is the temperature, and k is the thermal conductivity. This figure of merit reflects the fact that less resistance to electric current (σ) and higher temperature will lead to greater efficiency as further illustrated by Equation (1) below.

However, it reflects a major challenge for thermoelectric materials research: the fact that thermal transport and electrical transport are positively related in most materials according to the Wiedermann-Franz law (Hendricks & Choate, 2006), so any materials with higher electrical conductivity (σ) also tend to have higher thermal conductivity (k).There is no theoretical limit to ZT, but best materials in common use today have values around 1 (Tritt, 2011). The relationship between ZT and efficiency for a thermoelectric element is expressed in Equation (1) where T_h and T_c are the temperatures on the hot and cold sides of the element respectively and T is the average of T_h and T_c (Tritt, 2011).

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h} \quad (1)$$

Equation (1) assumes that ZT for the average temperature is representative of the temperature range and a higher temperature gradient increases power efficiency. Given this equation with hot and cold side temperatures of 250°C and 50°C respectively, an increase of ZT from 1 to 3 would correspond with an efficiency increase from 11% to 19%, for the simplest device architecture i.e. not cascaded or segmented (see discussion later in this assessment).

2. Technology Assessment and Potential

2.1 Performance Advances

2.1.1 High ZT Materials

Advances in high ZT (greater than 1) thermoelectric materials research have been made in the last 20 years (Heremans, Dresselhaus, Bell, & Morelli, 2013). Among the uniform or bulk materials (materials with no intentional micro or nanostructuring including most current commercial thermoelectrics), the highest performing materials display phonon-glass electron-crystal behavior where phonons move through the crystal material behaving like a glass while electrons move through the material. The resulting reduction in thermal conductivity while increasing causes an increase in ZT as discussed earlier. Material features that can lead to this behavior include heavy elements and atoms or molecules in cage-like lattice structures that serve to scatter traveling phonons (Tian et al., 2013). However, the best compositions for traditional bulk thermoelectric materials had largely been discovered by 1980 (Heremans et al., 2013). Further improvements in ZT values were made possible as a result of research published by Hicks and Dresselhaus in 1993. They found that material nanostructure could lead to low dimensional quantum wells and phonon-scattering at grain boundaries that lowered thermal conductivity (Hicks & Dresselhaus, 1993). **Figure 1** (Heremans et al., 2013) shows that reported ZT results in literature had reached a plateau at the time that Hicks and Dresselhaus published their 1993 paper, and that these results began to climb afterward. In actual field applications, the best bulk ZT has been found around 1.3-1.5 and no one has been able to make ZT of 2.27 as noted in this figure. However, the techniques used to create nanostructure in thermoelectric materials are prohibitively expensive, and more research is required in order to bring down their cost to fully realize the gains in efficiency they allow (LeBlanc et al., 2014).

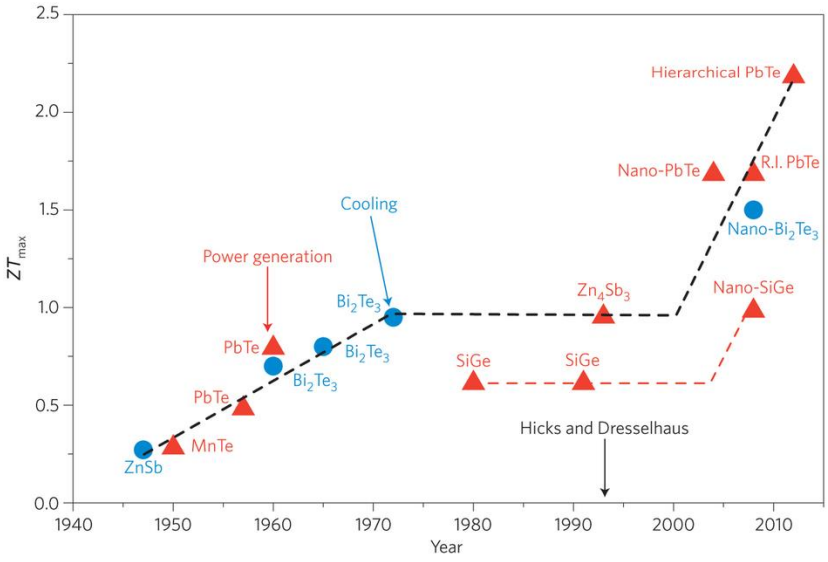

Figure 1 Progress in reported ZT values over time (Heremans et al., 2013)**.**

2.2 Potential for Improvement

2.2.1 High ZT Materials

High ZT Materials have been discovered in a number of materials systems in recent years and making them more efficient generation possible in laboratory settings. Some less commercially established material classes that have shown promising results include skutterudites, clathrates, Half-Heuslers, and oxides such as cobaltites and perovskites (Tian et al., 2013). Lowering the cost of production of these materials could lead to more cost-effective high efficiency thermoelectric waste heat recovery. Continued increases in ZT and other advancements in materials research and development are essential if thermoelectric waste heat recovery is to be common practice in the US. First, alternative materials must be developed because of potential issues with traditional materials. Low thermal resistance in combination with high electrical resistance, ability to withstand high temperatures, ZT limits, and thermal cycling are some of the major issues remain to be addressed. In addition, Lead is subject to numerous governmental regulations, and Tellurium markets could see dramatic changes in demand depending on the market for CdTe solar cells. Alternative material classes, previously mentioned in the section, provide other benefits as well. Half-Heusler materials can tolerate high temperatures (GMZ Energy Corporation, 2014a), and tetrahedrites (Lu & Morelli, 2013) and magnesium silicides (LeBlanc et al., 2014) have cost advantages over traditional materials. Less expensive approaches to creating nanostructure in thermoelectric materials are also required if high ZT materials are to become common. DOE/VTO-funded projects are working to develop, test, and demonstrate on an engine dynamometer and full scale vehicle, at least a 5 percent fuel economy increase with advanced TEGs using bulk thermoelectric materials (e.g., Skutterudite, Half-Heusler). These advanced TEGs will be commercially viable with improved manufacturing, and feasible for cost reduction at production of 100,000 units/year initially (Cleary, 2014; Jovovic, 2014; Salvador & Meisner, 2014).

2.2.2 Low-Cost Materials

Some thermoelectric materials such as silicides (LeBlanc, Yee, Scullin, Dames, & Goodson, 2014), and tetrahedrites (Lu & Morelli, 2013) are primarily considered for their relatively low cost. Information about some of these material families is shown in **Table 1.** Maximum ZT and corresponding temperature data are from (Seshadri Group, 2013), efficiency is based on maximum ZT for ΔT of 600 °C, and material cost data is from (LeBlanc et al., 2014).

Table 1. Properties, materials/device efficiency, and cost for different families of thermoelectric materials (LeBlanc et al., 2014; Seshadri Group, 2013).

Material Family	Max ZT	Temp (°C)	Efficiency	Average Material Cost ($/kg)
Cobalt Oxide	1.4	727	12%	$345
Clathrate	1.4	727	12%	$5,310
SiGe	0.86	727	9%	$6,033
Chalcogenide	2.27	727	16%	$730
Half -Heusler	1.42	427	17%	$1,988
Skutterudite	1.5	427	18%	$562
Silicide	0.93	727	9%	$151

The costs shown are based on estimates that don't take into account economies of scale, so if any of these materials became widely used, prices would likely fall (Saniya LeBlanc, personal communication, September 9, 2014). Oxide materials such as cobalt oxide are not being used today as there are limited n-type oxide with similar structures as p-type cobalt oxide that can be made. When an oxide TEG system is attempted, the best ZT values reported are around 0.3. More common use of these materials and improvement of their thermoelectric performance could lead to thermoelectric generation that would be cost-competitive with grid electricity.

When taking a broader perspective of TEGs, the share of material cost is significantly high, i.e., in the range of 50-80% to the overall thermoelectric system generation cost (LeBlanc et al. 2014). As shown in **Table 2**, the cost of thermoelectric generation today is many times greater today than other competing technologies such as coal, natural gas, geothermal, and photovoltaics. The system cost figures are based on several underlying assumptions such as equivalent properties in p and n-type materials discussed in (LeBlanc et al., 2014). Due to poor economics, total thermoelectric market of $45 million for energy harvesting has been limited to military and aerospace markets today (Das, 2012). An early application of thermoelectric generation was pioneered by the NASA Jet Propulsion Laboratory which used thermoelectrics with nuclear power sources for spacecraft power systems and thermal control for various space exploration missions. In August of 2012, the NASA Mars Science Laboratory -- Curiosity Rover (Jet Propusion Laboratory, 2015), powered by a multi-mission radioisotope thermoelectric generator (MMRTG) (Caponiti, 2008), landed on Mars. One of the target applications of thermoelectric power generation is to power wireless sensor networks, particularly in buildings, and the total market size is expected to reach $25 million by 2016 (Zervos, 2014). It is projected that the total market for thermoelectric energy harvesters will reach over $950 million by 2024 (Zervos, 2014).

Table 2. A cost comparison of competing power generation technologies (LeBlanc et al. 2014)

Application Temperature	Power Generation Technology	System Cost ($/W)
Low ($T_h \approx 100$ °C)	Geothermal	$4.14
	Half-Heusler Thermoelectric (Bulk $Zr_{0.25}Hf_{0.25}Ti_{0.5}NiSn_{0.994}Sb_{0.006}$)	$125.05
	Silicon Nanowire Thermoelectric	$104.18
	Chalcogenide Thermoelectric (Nanobulk $Bi_{0.52}Sb_{1.48}Te_3$)	$62.44
Medium ($T_h \approx 250$ °C)	Organic Rankine Cycle	$4.00
	Concentrating Solar Power	$3.60
	PV Target	$1.00
	Skutterudite Thermoelectric (Bulk $Yb_{0.2}In_{0.2}Co_4Sb_{12}$)	$19.02
	Half-Heusler Thermoelectric (Bulk $Zr_{0.25}Hf_{0.25}Ti_{0.5}NiSn_{0.994}Sb_{0.006}$)	$14.45
	Chalcogenide Thermoelectric (Nanobulk $Bi_{0.52}Sb_{1.48}Te_3$)	$11.92
High ($T_h \approx 500$ °C)	Nuclear	5.34
	Coal	$2.84
	Natural Gas	$0.98
	Silicide Thermoelectric (Bulk $Mg_2Si_{0.6}Sn_{0.4}$)	$5.56
	Chalcogenide Thermoelectric (Bulk $AgPb_{18}SbTe_{20}$)	$5.06
	Half-Heusler Thermoelectric (Bulk $Zr_{0.25}Hf_{0.25}Ti_{0.5}NiSn_{0.994}Sb_{0.006}$)	$4.48

2.2.3 High Temperature Modules

Thermoelectric generation is usually accomplished by means of thermoelectric couples as shown in **Figure 2**. Small legs of p-type (blue) and n-type (red) thermoelectric elements are connected in series and then sandwiched between insulating ceramic substrates. These couples are most often arranged into a planar package called a thermoelectric module. Thermoelectric generator systems are composed of these modules, as well as additional equipment design features to move heat and electricity through the system. Because thermoelectric efficiency increases with temperature, recent advances in high temperature thermoelectric modules are showing promise. Half-Heusler alloys, which contain varying quantities of nickel, tin, zirconium, titanium, and hafnium (Tritt, 2011), and which can sustain generation at temperatures higher than the 583 °C melting point of bismuth telluride, seem particularly close to a

market breakthrough. GMZ has produced a module using Half-Heusler materials that they claim can operate continuously exposed to a hot side temperature of 600 °C and a cold side temperature of 100 °C (GMZ Energy Corporation, 2014b). Under these conditions it is advertised to produce 15.3 W from a 16 cm^2 area. Novus Energy Technologies is developing a competing high temperature module also using Half-Heuslers that they project could produce 55 W from the same area and could cost as little as $0.10/W with highly automated production at scale (Peter Thomas, personal communication, September 9,2014).

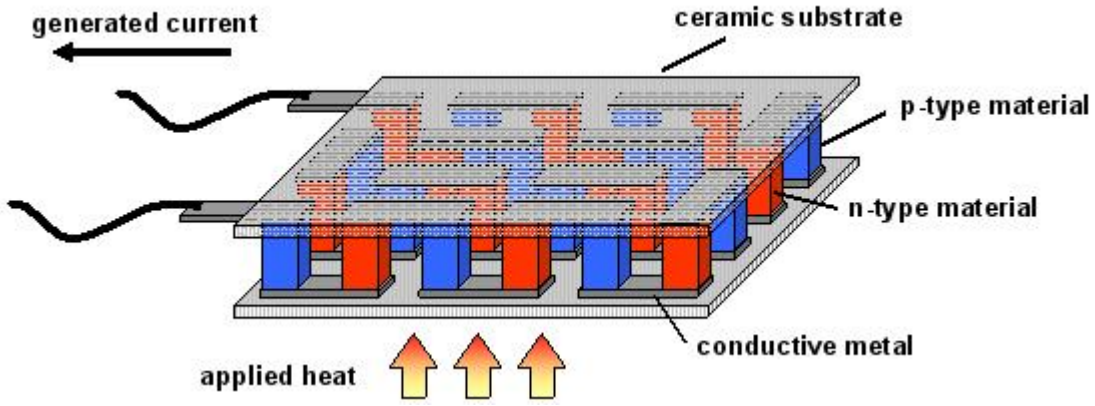

Figure 2. Schematic diagram of a typical thermoelectric module (SIGMA-ALDRICH, 2015)

2.2.4 Cascading Modules

Better thermoelectric assembly techniques could enable easier construction of cascaded thermoelectric generators. Cascaded generators are meant to better match TE materials to their optimum temperature gradients and thereby its efficiencies, but by stacking modules with different materials, rather than subdividing the module legs as in segmented modules. One particular advantage of cascaded thermoelectric generators not shared by segmented generators is that at each stage of a cascaded thermoelectric device, a separate electric circuit can be implemented. Avoiding the inherently serialized circuit in a segmented device allows for higher efficiencies, but also leads to greater system complexity (Snyder & Ursell, 2003). The overall conversion efficiency of cascade-type module roughly becomes the sum of the values of efficiency of the individual modules. Some cascaded thermoelectric modules are commercially available, but their potential can be expanded with more research and development. Using three-stage cascade-type modules consisting of high-end ZT values of $Ca_3Co_4O_9$ for p-type elements and $SrTiO_3$ for n-type elements, an overall thermoelectric generation efficiency of 20% has been estimated (Fujisaka, T. et al. 2013).

2.2.5 Segmentation

In addition to advances in individual materials, thermoelectric performance might be improved by techniques like dividing thermoelectric legs into segments (Hadjistassou, Kyriakides, & Georgiou, 2013). Materials for each segment can be chosen based on what materials have the highest ZT for the temperature in that part of the leg. This optimization of ZT over the entire thermal gradient would result in a higher effective ZT for the thermoelectric module and thus higher electrical generation efficiency.

Making thermoelectric legs with different material segments would obviously make module manufacturing more expensive, but could be applicable in applications like remote generation where efficiency and reliability would be at a premium. Segmented thermoelectric modules are often discussed in literature, but they are not in common use for energy harvesting applications. This module type requires manufacturing techniques that would currently be too expensive. More research and development work could allow segmentation techniques to become cost- effective and lead to commercialization of this efficiency-improving technology.

2.2.6 Demonstrations

Demonstrations of high power thermoelectric waste heat recovery are necessary to prove that such systems can take advantage of economies of scale. Demonstrated power has typically been less than 1 kW, with notable demonstrations of 169 W generation from a cement kiln (Hsu, Won, Chu, & Hwang, 2013), 250 W generation from glass furnace exhaust (Polcyn & Khaleel, 2009), and 240 W generation from a steel carburizing furnace afterburner (Kaibe, Kajihara, Fujimoto, Makino, & Hachiuma, 2011). Two recent thermoelectric energy harvesting efforts have demonstrated power generation in excess of 1 kW. The first of these involved a high power TEG installed over a continuous casting line. This system contained 896 Komatsu modules –16 of which were used in the aforementioned carburizing furnace demonstration, and it produced power on the order of 9 kW when exposed to the radiant heat of a 915 °C slab (Kuroki et al., 2014). The other is the first plug-and-play thermoelectric generator available for purchase, the 25 kW Alphabet Energy E1 which was announced in October 2014 (EE Times India, 2014).

2.2.7 Assembly

Progress must also be made in the area of automated assembly so that thermoelectric devices can be made in a reliable and cost-effective manner. Traditionally the legs are soldered to metal interconnects by hand and those interconnected legs are then mounted on a plate of insulating material such as a ceramic (Hendricks & Choate, 2006). Gerard Campeau of Thermal Electronics Corporation claimed that 90% of thermoelectric modules are still assembled by hand (personal communication, April 11, 2014). Some more advanced manufacturers have implemented automation systems for this assembly process, but in most cases, price points don't justify straying away from the standard pick and place machines used to assemble electronic components (Saniya LeBlanc, personal communication, September 9, 2014). Thin film thermoelectric modules offer an alternative to the manufacturing methods of conventional bulk materials as the p- and n-type materials can be sputtered onto separate wafers—using techniques from silicon microelectronics fabrication—that are then fused together.

2.3 System Integration Needs

2.3.1 Thermal Management

More research is needed into heat transfer in thermoelectric generators. This includes cost optimization of heat exchangers that collect source heat and transfer heat to cooling water, but it also would include heat transfer within the module. Costs for electrically insulating plates (usually ceramic) must be reduced while maintaining good thermal conductivity. Electrical interconnects and other interfaces must be engineered to maximize device reliability and thermal conductivity. Using more corrosion resistant heat exchangers would allow thermoelectric heat recovery from a more diverse range of industrial

exhaust streams. Studies to co-optimize the thermal and electrical properties of the whole TEG system while maintaining its mechanical integrity are also important (Yazawa & Shakouri, 2010).

2.4 Technology Needs

An overarching technology need is to reduce the cost of power generated by thermoelectric waste heat recovery systems. This need can be met by using lower cost materials as well as by using better automated methods of thermoelectric assembly. A commonly discussed cost target in the thermoelectric field is 1 $/W for an installed system. This, along with a system life of only 5 years, a discount rate of 7%, a capacity factor of 75%, and an annual cost (for maintenance and operating costs) of 20 ¢/W would lead to a levelized cost of electricity of 6.7 ¢/kWh. This is comparable to the 2013 average U.S. industrial electricity price of 6.82 ¢/kWh (U.S. Energy Information Administration, 2014).

2.4.1 Manufacturing Challenges and Opportunities

Labor-intensive pick and place methodology is state of the art today. A recent DOE workshop on manufacturing opportunities for low-cost thermos-electric modules has indicated that labor is responsible for a significant portion of the cost of TE modules (U.S. DOE, 2014). New manufacturing approaches such as automation and wafer-based manufacturing have the potential to reduce TE module costs. Concepts discussed at the workshop include additive manufacturing of TE modules. One of the Fraunhofer Institutes demonstrated additive manufacturing of TE with embedded sensors (Fraunhofer, 2013). More demonstrations with medium and high T Thermo-electric materials are needed to prove this approach is viable.

2.4.2 Value-added Applications

Current technology can be cost- effective when the thermoelectric system adds value beyond electricity production, as is the case in generation for wireless sensor networks. TEGs combined with wireless sensor network nodes can add value to by allowing sensing and automation without the need for wire runs or batteries that require checking and replacement. Additionally, remote industrial facilities with abundant waste heat and expensive electricity—in the oil and gas industry, for example—might stand to benefit from current thermoelectric technology. Examples of these value additions outside of the manufacturing sector include the use of thermoelectrics to drive fans that increase the efficiency of woodstoves (Patyk, 2009) and to power wirelessly controlled radiator valves that don't need batteries. Hi-Z Technology, one of the major companies involved in thermoelectric generator research and development, has demonstrated woodstoves with TEG-powered fans to show the potential of TEGs to allow for self-powered appliances (Bass & Thelin, 2001).

2.5 Potential Impacts

2.5.1 Thermoelectric Waste Heat Recovery

The lack of moving parts in thermoelectric generators holds the promise of reduced O&M costs and longer time between failures. These potential benefits make thermoelectric generators important to consider for industrial waste heat recovery applications. Large-scale TEGs (greater than 1 kW) that generate general purpose power (i.e. power not meant for a particular dedicated application) from industrial waste heat, are not in general use at the time of this report. The largest commercially

available TEG systems are remote generators manufactured by Global Thermoelectric, a Calgary-based company recently acquired by Gentherm, which has installed over 20,000 TEGs. These systems are generally fuel burning with a maximum power around 500 W, and they provide electricity along gas pipelines and on offshore oil platforms, among other similar locations (Global Thermoelectric, 2012). However, there are a few larger waste heat systems that have been installed and discussed in literature. An extensive study of a thermoelectric generator in a working glass plant (Polcyn & Khaleel, 2009) — discussed the difficulty of delivering heat from the exhaust stream to the generator via a heat pipe. The power generation in this study was not cost effective, and the researchers faced great difficulties with degradation of heat flux through the heat pipe due to corrosion in the exhaust flue.

The iron and steel industry is a common target for waste heat recovery technology based on its high quality waste heat. As such, the iron and steel industry has seen some of the most extensive discussion of industrial thermoelectric waste heat applications in literature. One notable study involved a TEG with 16 bismuth telluride modules placed above an afterburner flame in the exhaust system of a carburizing furnace at a Komatsu steel plant in Awazu (Kaibe, Makino, Kajihara, Fujimoto, & Hachiuma, 2012). The afterburner flame was estimated to produce up to 20 kW of heat and to induce temperatures between 120 and 250 °C on the heat collection place of the water-cooled TEG. The modules used were developed by a Komatsu subsidiary, had a potential power density of 1 W/cm^2, and the highest conversion efficiency of any commercial TE module when they were announced in 2009 (KOMATSU Corporate Communications, 2009). The modules were very expensive, however, with a price of roughly $30/W when they were released. A later study at this plant has demonstrated power outputs on the order of 240 W for single generators, and discussed the installation of power hardware to effectively manage the output of multiple generators (Kaibe et al., 2014).

2.5.2 Emerging Alternatives to Thermoelectric Generation

Numerous alternative technologies for converting waste heat to have been proposed. Phase change material (PCM) engine generators use the volume changes caused by the melting and solidification of a PCM material like paraffin wax to drive a hydraulic system. That hydraulic power is used to drive a generator and produce electric power. A study of these systems found they had the potential for higher net present value than ORC systems at very low temperatures (60–75 °C) over a 20 year life (Johansson and Söderström, 2013). Magnetocaloric generators have high exergy efficiencies that would be useful in industrial waste heat recovery (Vuarnoz, Kitanovski, & Gonin, 2012). However, few magnetocaloric materials have been discovered, they are generally expensive, and they don't have the high Curie temperatures necessary for most waste heat applications. Thermal power can also be converted into vibratory mechanical power and then harvested on the macroscale using a thermoacoustic heat engine (Haddad, Périlhon, Danlos, François, & Descombes, 2014) or on the microscale using piezoelectric power generation (Hendricks and Choate, 2006). Heat can also be used to stimulate the emission of photons or electrons. Photons are emitted in thermophotovoltaic generation, discussed for automotive heat recovery in (Arnaud, Ludovic, Mouad, Hamid, and Vincent, 2014). Electron excitation drives thermionic generation which Melosh and Shen discuss as a means of improving the efficiency of solar photovoltaics (Melosh and Shen 2012). However these novel methods are unproven in industrial heat recovery at the

kilowatt scale and are currently not economically viable? such as piezoelectric generation (conversion of ambient vibrations, low-temperature waste heat 200-300F) is estimated to cost $10,000/W today.

2.5.3 National Recovery Potential

To obtain an estimate of the amounts of waste heat in each industrial sector, the AMO's Manufacturing Energy and Carbon Footprints data (Energetics Incorporated, 2014) were used. An initial estimate of the potential of thermoelectric energy harvesting from the waste heat of manufacturing plants can be obtained by choosing some fraction of the heat that can be recovered by generation systems, and then estimating an efficiency value for those systems. The choice for the low end of the recoverable heat range was 10% based on an estimate from (Polcyn & Khaleel, 2009), and the high end of 25% was based on heat recovery calculations for boiler exhaust from (Hill, 2011). The results for such an estimate can be seen in **Table** with the recoverable heat as a range from 10% to 25% of the sector's process heating losses and the thermoelectric generation efficiency assumed to be 5%. Five percent is a fairly typical efficiency value given current thermoelectric technology. The thermoelectric recovery potential for all of US manufacturing in this estimate is 6.5–16.4 TWh of electrical energy for 2010 which is 0.9–2.3% of the 712 TWh of on-site electrical energy used in US manufacturing plants that year. This is 1.5–3.7% of the 433 TWh of waste heat predicted for the 2,473 TWh worth of annual industrial energy consumption in BCS Incorporated's report for the DOE's Industrial Technology Program (Johnson et al., 2008).

Table 3. Thermoelectric generation potential estimates by major industrial sectors based on (Energetics Incorporated, 2014).

Manufacturing Sector	Process Heating Energy Use (TBtu)	Process Heating Energy Loss (TBtu)	Recoverable Heat (Min–Max) (TBtu)	TE Potential (Min–Max) (GWh)
Petroleum Refining	2,250	397	40–99	582–1,454
Chemicals	1,455	328	33–82	481–1,201
Forest Products	980	701	70–175	1,027–2,567
Iron and Steel	729	334	33–84	489–1,223
Food and Beverage	518	293	29–73	429–1,073
Cement	213	84	8–21	123–308
Glass	161	88	9–22	129–322
Fabricated Metals	139	49	5–12	72–179
Transportation Equipment	65	23	2–6	34–84
Foundries	61	28	3–7	41–103
Plastics and Rubber	88	20	2–5	29–73
Textiles	40	23	2–6	34–84
Alumina and Aluminum	81	37	4–9	54–136
Computers, Electronics, & Electrical Equipment	42	15	2–4	22–55
Machinery	37	13	1–3	19–48
All Manufacturing	**7,204**	**2,567**	**447–1,117**	**6,547–16,368**

2.5.4 Steel Industry Potential and Cost

Results for a modified version of a cost model from (LeBlanc et al., 2014) for thermoelectric generation system costs and the resulting LCOE values have been used to evaluate the economics of thermoelectric generation in the steel industry based on a detailed waste heat breakdown. These results are shown in **Table 4** for both the optimistic price calculations that used theoretical module cost per watt figures, and the pessimistic price calculations that used a module cost per watt based on the prices of modules currently on the market. Grey backgrounds represent exhaust sources while white backgrounds represent non-exhaust sources. The underlined sources—castings, basic oxygen furnaces, and blast furnaces/stoves—are deemed the most promising for thermoelectric waste heat recovery. These are the non-exhaust waste heat sources with the lowest LCOE values. Non-exhaust waste heat sources are desirable because the corrosive chemicals in steel industry exhaust gases are a great obstacle to thermoelectric waste heat recovery.

347 **Table 4.** Estimated system cost and electricity price predictions based on cost model (LeBlanc et al., 2014) results for various waste heat sources
348 within the steel industry.

							Based on market module costs (pessimistic)		Based on theoretical module costs (optimistic)	
Plant type	2010 US production (Mtons)	Heat source	Avg temp (°C)	TEG efficiency Tc = 35 °C	TEG output (kBtu/ton)	2010 TEG output (GWh)	Initial System cost ($/W)	15—5 yr LCOE ($/kWh)	Initial System cost ($/W)	15—5 yr LCOE ($/kWh)
Integrated	34.3	Coke oven	527	3%	4—7	37—73	$12	$0.24—0.44	$5	$0.11—0.20
			586	2%	0.4—0.8	4—8	$28	$0.57—1.05	$14	$0.28—0.52
		Blast furnace/ Blast stove	192	1%	2—4	22—43	$78	$1.59—2.92	$40	$0.88—1.62
			1472	3%	6—12	61—122	$8	$0.17—0.31	$4	$0.08—0.14
		BOF	1341	3%	2—4	19—37	$7	$0.14—0.26	$3	$0.06—0.11
			1520	4%	0.6—1.2	6—12	$8	$0.16—0.30	$4	$0.07—0.14
Mini-mill	54.4	EAF	1110	4%	7—13	107—214	$7	$0.14—0.26	$3	$0.06—0.11
			1110	3%	0.5—1.0	8—15	$11	$0.22—0.40	$5	$0.10—0.18
Cross-sector	88.7	Casting								
			1600	4%	2—4	46—91	$8	$0.16—0.29	$4	$0.07—0.13
		Hot rolling	900	4%	3—6	28—56	$7	$0.15—0.27	$3	$0.07—0.12
			900	3%	3—5	27—54	$14	$0.28—0.52	$6	$0.13—0.24
		Finishing/ Heat Treating/ Annealing	500	3%	2—3	17—34	$13	$0.26—0.48	$6	$0.12—0.22
			500	1%	0.5—1.0	5—11	$37	$0.74—1.37	$19	$0.38—0.70
Exhaust total				**2.7%**	**12—23**	**229—281**	**$15**	**$0.30—0.56**	**$7**	**$0.15—0.28**
Non-exhaust total				**2.8%**	**8—16**	**157—221**	**$11**	**$0.22—0.40**	**$5**	**$0.10—0.19**
Total				**2.7%**	**20—39**	**386—772**	**$13**	**$0.27—0.49**	**$6**	**$0.13—0.24**

3. Program Considerations to Support R&D

3.1.1 Research and Development

Discussions with the industry leaders indicate that one way that DOE could encourage the adoption of thermoelectric waste heat recovery by manufacturers would be to create and promote uniform performance standards and metrics by which to measure thermoelectric materials and devices. Materials standards, standard materials testing, and device testing procedures are critical to the commercialization of thermoelectrics as power generation devices. Better standards would increase manufacturer confidence in the technology with a resulting significant higher potential of market growth. Round robin testing of thermoelectric materials by companies and government labs to develop reliable and confirmed properties is a positive step in this direction (Wang et al., 2013).

Another way that government could drive thermoelectric innovation is by establishing shared use facilities for some of the more expensive nanostructuring technologies used for TE materials. This would allow smaller companies requiring a lower level of investment with a limited manufacturing design capability to enter the market, develop improved device processing steps, and produce devices at lower costs. It could have an impact similar to the fabless foundry model in silicon microelectronics, encouraging innovation and decreasing upfront costs.

There have been great incremental improvements in thermoelectric materials over the past 20 years but they are often been overshadowed by unconfirmed claims and publications. Technologies and materials solutions to improve interface contact resistance are very important to reduce interfacial losses thereby maximizing the performance. The opportunity for a breakthrough in thermoelectric material exists to demonstrate a substantial improvement in ZT value. System-level development requiring a large level of investment is necessary alongside the material development activities supported by government investments.

3.1.2 Public/Private Research Efforts

There has been a great deal of collaboration between public institutions and private companies toward thermoelectric research. The DOE Vehicle Technologies Office (VTO) has advanced the development of vehicular thermoelectric generators (TEGs). An early DOE-funded project successfully developed a TEG demonstrator unit using bismuth telluride cells integrated with the muffler of a long-haul truck. This provided impetus for continued work to develop advanced TEGs to harvest the energy in the hot engine exhaust (300 to 600 °C) to improve the overall fuel economy and reduce emissions from passenger and commercial vehicles. Subsequent projects successfully completed design, fabrication, and installation of prototype TEGs into production vehicle platforms to demonstrate feasibility (Fairbanks, 2013). DOE/VTO also leverages thermoelectric materials expertise in academia through partnership with the National Science Foundation (NSF). DOE and NSF provided grants to selected university teams to develop cost-competitive automotive thermoelectric materials and manufacturing techniques (Jovovic, 2014). Advances achieved in these projects will help to foster thermoelectric developments for other uses

including industrial applications (Goodson, Kozinsky, & Nolas, 2013; Heremans, Kanatzidis, Lu, Bell, & Kossakovski, 2012; Huxtable, Ekkad, Priya, & Miner, 2012).

Internationally, Japanese applications research has been extensive, involving organizations like New Energy and Industrial Technology Development Organization (NEDO) and National Institute of Advanced Industrial Science and Technology (AIST), and including trials in working steel plants (Kaibe et al., 2012; Kuroki et al., 2014). European programs NEAT and NEXTEC mention industrial applications as goals, but have not produced any significant developments in that space. NEAT aims to develop a nanocomposite material that can be produced in bulk and achieve a ZT greater than 3. NEXTEC is meant as a demonstration project involving nano-engineered materials (Kuznetsov, 2014).

3.1.3 Applications

DOE could encourage adoption of waste heat recovery in manufacturing (using TEGs or other technologies), by pushing for higher efficiency standards for manufacturing facilities. These could drive the adoption of high efficiency manufacturing technologies in the same way that CAFE standards do for automobiles. Thermoelectric demonstration at the levels of prototype and scale-up production is necessary since a 10-20% decrease in ZT is quite common at a large production volume due to possible process defects. There is no large volume thermoelectric material producer in the world today. Collaboration with manufacturers to perform cost-effective system-level TEG demonstrations in near-term potential applications like those performed in Japanese steel plants (Kaibe et al., 2012; Kuroki et al., 2014) would also be useful for establishing the efficacy of TEG waste heat recovery. Finally, encouragement of wireless sensor network energy data collection could show manufacturers which of their systems produce the most sensible and latent heat for waste heat recovery. Encouraging the use of self-power TEG sensor nodes would have the added benefit of increasing the exposure of TEG technology.

4. Risk, Uncertainty, and other Considerations

Risks involved in encouraging research and development in thermoelectric waste heat recovery fall into three categories: those related to the effectiveness (efficiency, power, and durability) of thermoelectric generators, those related to competing technologies, and those related to the amount of waste heat available. Thermoelectric generation could be found ineffective if TEGs never reach a low enough price point for wide adoption. A frequently discussed cost target for thermoelectric generation is $1/W which, given a fairly conservative set of assumptions discussed earlier, would lead to electricity costs competitive with the average cost of electricity for US industrial use in 2013: 6.82 ¢/kWh (U.S. Energy Information Administration, 2014). Thermoelectric generators might also be found to degrade when exposed to variable temperature environments over multi-year lifespans. Other countries could also have advantages in thermoelectric production due to their extant research base (Japan) or manufacturing infrastructure (China, Vietnam). Other technologies for waste heat recovery like low temperature Rankine cycle variants, load preheating, or exotic solutions like phase change material generators could see breakthroughs that would cause them to outcompete TEGs. Preheating and Rankine cycle variations are more commercially established than TEGs as industrial waste heat recovery solutions, but thermoelectrics have advantages of minimal maintenance requirements, as well as option

to install with minimal downtime and minimal effects to existing systems. Finally, if higher efficiency industrial processes are adopted or value chains change to lower waste heat options (integrated steel mills to mini-mills for example) then the amount for waste heat available for thermoelectric recovery would decrease, leading to less of a return on thermoelectric R&D investment.

5. Sidebars

5.1.1 Nucor Mini-mill in Jewett, Texas

The possibilities for installing a similar system to the one described at a JFE plant in (Kuroki et al., 2014) at the Nucor mini-mill in Jewett, TX were explored. The five continuous casting lines at this plant produce strands that—at 13–30 cm wide—are not as wide as the 1.3–1.7 m slabs at the JFE plant, but assuming that the slab temperatures are the same, a similar amount of heat flux (on the order of 17 $kW_{thermal}/m^2$) could be achieved by placing 50 cm wide generators roughly 20 cm from the cast slabs. Assuming that the same level of thermoelectric generation per unit area that (Kuroki et al., 2014) discussed (1.13 $kW_{electric}/m^2$) could be achieved over 14 meters for each strand, 39 $kW_{electric}$ of thermoelectric power could be produced by 35 m^2 of generators (based on a 14 m × 0.5 m generator above each of 5 strands) at the Nucor plant. Under these conditions, using a nanobulk $Bi_{0.52}Sb_{1.48}Te_3$ TEG of a higher ZT value of 1 with a 15-year lifespan and a capacity factor of 60%, a modified version of the cost model from (LeBlanc et al., 2014) predicts a levelized cost of electricity of 31 ¢/kWh. A complete cost estimate breakdown of this along with a cost comparison using a bulk module Mg2Si0.6Sn0.4 of a lower ZT value of 0.3 are discussed in Appendix.

5.1.2 Alphabet Energy

In October of 2014, Alphabet Energy announced a product called the E1 that fits in a standard shipping container, connects to the exhaust pipe of a generator, and has a modular design so that thermoelectric components can be swapped out as materials improve. The thermoelectric materials used in the E1 are p-type tetrahedrites, and n-type magnesium silicide (Mg_2Si) which will provide the average ZT of around 1 similar to that obtained by skutterudite (GM, Gentherm) and half-heusler (GMZ) materials used by the DOE Waste Heat 2 (WH2) projects (Matthew Scullin, personal communication, October 27,2014). The company claims that the E1 can produce 25 kW from the exhaust of a 1000 kW generator (Lamonica, 2014) implying an efficiency of about 2.5% based on the exhaust heat of such a generator (Caterpillar, 2013). If running constantly, the generator would produce roughly 748 MBtu per year, saving more than 50,000 liters of diesel fuel per year.

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7. APPENDIX

8. Nucor Mini-Mill, Jewett, Texas: Thermoelectric Generation Potential Economics

A cost model based on (LeBlanc et al., 2014) was used to determine potential costs for such a system. This application of the model could be more detailed because in this case the heat flux was known, as was the fact that the temperature difference over the modules should be about 200 °C as stated in Kuroki et al. (2014). Radiation heat transfer calculations led to heat flux agreement when the exterior temperature of the hot side heat exchanger is 330 °C, and it is known that the temperature of the cooling water is 35 °C. Additionally, the heat exchanger U-values in the 100–120 W/m^2-K range used in LeBlanc et al. (2014) and previously in this report would not achieve a module ΔT of 200 °C given a system ΔT of 295 °C. Thus the U-values for the heat exchangers were increased to 500 W/m^2-K to reflect the lower thermal resistance between the heat exchanger boundaries and the thermoelectric material. Given these inputs and set of material properties, various combinations of fill factor and leg length input parameters could be examined until an appropriate heat flux is achieved. The inputs and outputs for the simulated Nucor continuous casting line facility with Bulk $Mg_2Si_{0.6}Sn_{0.4}$ thermoelectric properties are shown in **Table 5.**

Table 5. List of major input and output parameter values for application of cost model (LeBlanc et al., 2014) for the Nucor TEG system with bulk $Mg_2Si_{0.6}Sn_{0.4}$ modules.

Inputs				Outputs	
Parameter (unit)	**Value**	**Parameter (unit)**	**Value**	**Parameter (unit)**	**Value**
L (mm)	11.5	**ρ (kg/m^3)**	4166	**Module ΔT (°C)**	225
F (%)	20	**C_B ($/kg)**	127.51	**Power (W/m^2)**	625
m	1	**$C_{M,B}$ ($/kg)**	0	**Heat flux (kW/m^2)**	17.6
T_h (°C)	330	**$C_{M,A}$ ($/m^2)**	168.23	**TE material cost ($/m^2)**	1255
T_c (°C)	35	**$C_{HX,ceramic}$ ($/[W/K])**	2	**Ceramic cost ($/m^2)**	1000
S (V/K)	-0.00014	**$C_{HX,external}$ ($/[W/K])**	5	**Ext. Heat Ex. Cost ($/m^2)**	2500
σ (S/m)	154131	**U_{hot} (W/m^2-K)**	500	**η (%)**	3.6
k (W/m-K)	3.08	**U_{cold} (W/m^2-K)**	500	**G ($/W)**	7.61

The target generation rate could not be achieved with this material because of its relatively low ZT value of 0.3. However $Mg_2Si_{0.6}Sn_{0.4}$ still produces one of the lowest theoretical costs because the material is so inexpensive. The 15-year LCOE resulting from this test along with $2 of additional expenses and the known capacity factor of 60% is 29 ¢/kWh.

A material with a higher ZT (1 vs. 0.3) at the relevant temperatures could achieve the targets of both electrical generation as well as heat flux. One such material is nanobulk $Bi_{0.52}Sb_{1.48}Te_3$ with a ZT of 1 under these conditions. Inputs and outputs for such a TEG system application using a higher ZT material are shown in **Table 6**.

Table 6. List of major input and output parameter values for application of cost model (LeBlanc et al., 2014) for the Nucor TEG system with nanobulk $Bi_{0.52}Sb_{1.48}Te_3$ modules.

Inputs				Outputs	
Parameter (unit)	**Value**	**Parameter (unit)**	**Value**	**Parameter (unit)**	**Value**
L (mm)	5	**ρ (kg/m^3)**	6900	**Module ΔT (°C)**	226
F (%)	25	**C_B ($/kg)**	829.06	**Power (W/m^2)**	1295
m	1	**$C_{M,B}$ ($/kg)**	2.03	**Heat flux (kW/m^2)**	17.8
T_h (°C)	330	**$C_{M,A}$ ($/m^2)**	168.23	**TE material cost ($/m^2)**	7210
T_c (°C)	35	**$C_{HX,ceramic}$ ($/[W/K])**	2	**Ceramic cost ($/m^2)**	1000
S (V/K)	0.00023	**$C_{HX,external}$ ($/[W/K])**	5	**Ext. Heat Ex. Cost ($/m^2)**	2500
σ (S/m)	39060	**U_{hot} (W/m^2-K)**	500	**η (%)**	7.30
k (W/m-K)	0.81	**U_{cold} (W/m^2-K)**	500	**G ($/W)**	8.27

The 15-year LCOE for this higher cost ZT material in addition to the consideration of $2/W of additional expenses and the known capacity factor of 60% is 31 ¢/kWh. This is obviously better than the cost per watt for the system in Kuroki et al. (2014), but the price is still not competitive with the current grid-

646 based electricity price of 8 ¢/kWh at the Nucor plant. The detailed economic analysis has thereby
647 further confirmed that significant breakthroughs are needed before electricity produced with
648 thermoelectric generation systems can be competitive with electricity purchased from the grid.

649